The temperature behaviour of a ferroelectric smectic mixture and the detection of ferroelectric switching by NMR

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The temperature behaviour of a ferroelectric smectic mixture and the detection of ferroelectric switching by NMR

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The orientational order of a ferroelectric mixture has been measured by proton NMR. The alignment of the mesogenic units is reflected in the splitting of the NMR signal into a doublet. Up to a cell thickness of 200 μm, it was possible to produce well-oriented layers in the bookshelf geometry by magnetic orientation of the substances in the B_0-field. The angular dependences of the line width of the NMR signal on the tilt angle of the director have been calculated. A ferroelectric switching was detected by measuring the angular dependence of the line width in the switched state. The tilt angle and the orientational order parameter S of the bookshelf samples were estimated at various temperatures.

1. Introduction

Ferroelectric liquid crystals (FLCs) can undergo spontaneous polarization in an electric field so that the lateral dipole moments of the molecules align macroscopically along the same direction. They have attracted considerable attention since Clark and Lagerwall [1A] demonstrated that the ferroelectric property can be utilized for electro-optical displays [1, 2]. The properties of bistability and short response time make them very promising material for display and switching devices. Practically all applications of ferroelectric liquid crystals involve the creation of sufficient perfectly oriented structures.

Moreover, most of the methods for investigating the LC require that a monodomain structure has been established. Therefore, it seems to be a matter of crucial importance that a method is found for the reliable assessment of the perfection of the orientational structure. NMR appears to be one of the methods to fit this purpose [3]. It should be noted that the order parameters measured in the NMR procedures refer to the mesophase aligned in the strong magnetic field of the NMR instrument. In this regard, NMR methods are preferable to others such as measurement of the diamagnetic anisotropy or the IR dichroism, etc. The latter methods average over the entire sample. The coexistence of the isotropic and the cholesteric (or nematic) phase causes the sample to be not exactly aligned and thus leads to a lower value of the estimated order parameters [4].

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The aim of the published work is to describe the degree of order in magnetically pre-oriented ferroelectric liquid crystal cells in the bookshelf geometry by proton NMR.

For investigating ferroelectric switching, surface stabilized ferroelectric liquid crystal (SSFLC) cells are commonly used [5–7]. The thickness of SSFLC cells is in the range of some microns. However, the lower limit of the sample thickness in the NMR measurement is about 20 μm. The interaction between the modified surface and the first monolayer of the mesogens is generally too weak to align a sample up to this thickness. Therefore, SSFLC cells are unsuitable for NMR experiments.

We had already fabricated planar cells using a field stabilized ferroelectric liquid crystal and could show the possibility of detecting a ferroelectric switching by proton NMR. In one experiment it should therefore be possible to measure the orientational order parameter S of the pre-oriented layer, the ferroelectric switching and the tilt angle of the mesogenic units in the ferroelectric mesophase by using a model substance such as ZLI-3654.

2. Theoretical

Proton NMR is preferred for its high sensitivity which is of special importance in the case of investigations of thin layers in relatively low magnetic fields. Low magnetic fields are indeed necessary in order to avoid dominating magnetic effects in comparison with electric effects in *in situ* experiments near the clearing temperature.

The NMR resonance line for the simplest case of a two-proton system is a doublet according to the two

orientations of a proton dipole in the B_0-field. The dipolar splitting is given by:

$$\Delta v = \frac{3\mu_0}{8\pi^2} \frac{\gamma^2 \hbar}{\langle r^3 \rangle} S_{ij}^{\alpha\beta} \qquad (1)$$

with the magnetic constant μ_0, the gyromagnetic ratio of protons γ and $\hbar$, Planck's constant divided by 2π, and the internuclear separation r. Let (a, b, c) be the three orthogonal unit vectors linked to the molecule, so that the degree of alignment may be defined by the quantities (often called the 'ordering matrix')

$$S_{ij}^{\alpha\beta} = \frac{1}{2} \langle 3 i_\alpha j_\beta - \delta_{\alpha\beta} \delta_{ij} \rangle \qquad (2)$$

where $\alpha, \beta = x, y, z$ are indices referring to the laboratory frame – see figure 1, while $i, j = a, b, c$, and $\delta_{\alpha\beta}$ and δ_{ij} are Kronecker symbols. The brackets $\langle \ \rangle$ represent a thermal average [8].

Maier–Saupe theory assumes high symmetry for molecules forming liquid crystals. In reality, this is usually not the case and the theory has been extended to lath-like molecules [9]. For a biaxial molecule in a uniaxial phase in the principal axis system (x, y, z), only two order parameters, S_{zz} and $D = S_{xx} - S_{yy}$, are needed to describe the order, where

$$S_{zz} = \frac{1}{2}(3\cos^2 \theta - 1) \qquad (3)$$

$$D = S_{xx} - S_{yy} = \frac{1}{2}(3\sin^2 \theta \cos 2\alpha), \qquad (4)$$

which are related to the Wigner matrices according to [10] and the dipolar splitting becomes:

$$\Delta v = \frac{3\mu_0}{16\pi^2} \frac{\gamma^2 \hbar}{\langle r^3 \rangle} \left[S_{zz} + \frac{1}{3}(S_{xx} - S_{yy}) \right] \qquad (5)$$

where θ is the angle between the molecular long axis and the *para*-axis of the benzene rings. $D = S_{xx} - S_{yy}$ is directly associated with the Eulerian angle α made by
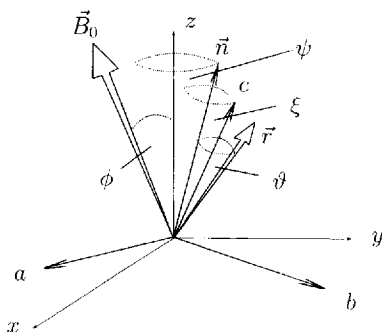

Figure 1.   The molecular frame (a, b, c) and the principal axis system (x, y, z).

the internuclear vector r in the principal axis system of the Saupe ordering matrix.

The mesogenic units are more or less rigid molecules with a small angular deviation of the proton internuclear vector r relative to the long axis of the molecule. The angle θ has a value not larger than 10 degrees. In this situation $D = S_{xx} - S_{yy}$ is negligible compared to S_{zz} [11]. Therefore, we can assume uniaxiality of the molecule.

Some smectic phases, like smectic C, and biaxial nematics exhibit phase biaxiality. Phase biaxiality may be described by a set of microscopic order parameters, when the mesogen is a rigid uniaxial particle. A value of the so-called phase biaxiality term D smaller than 0.08 was found by using the results of deuterium NMR [12].

Some treatments of NMR spectra have used a single S_{zz} approximation by ignoring the small contribution due to the $S_{xx} - S_{yy}$ [13, 14]. To interpret our results, we have used the uniaxial phase model of transverse isotropy, i.e.

— there is an anisotropic reorientation of the molecule around the molecular long axis c
— the axes c of the molecules are distributed on a cone around the director n
— the director distribution is axially symmetric around a preferred axis z in the sample, preferably the initial direction of orientation or the normal of the smectic layers.

Therefore, $S_{zz} = S$ can be obtained from the dipolar splitting of the resonance line (ϕ is the angle between B_0 and a preferred axis in the sample):

$$\Delta v = \frac{3\mu_0}{8\pi^2} \frac{\gamma^2 \hbar}{\langle r^3 \rangle} \frac{1}{2}(3\cos^2 \phi - 1)S \qquad (6)$$

If the director of the sample is aligned parallel ($\phi = 0°$) to the B_0 field direction, the orientational order parameter S and the main splitting Δv of the resonance line are simply related by:

$$\Delta v / \text{kHz} \approx 25.44 S. \qquad (7)$$

In the case of an unsplit line, it is possible to calculate the S parameter from the factor before the $(3\cos^2 \phi - 1)$ term in equation (6) by measuring a complete angular dependence of the line width Δf in the range from $\phi = 0°$ up to $\phi = 90°$. The measurement of orientational order parameters in this way is described elsewhere [15, 16].

3.   Experimental

The material investigated here is a commercial ferroelectric smectic liquid crystal mixture with the trade name ZLI-3654. It was first described and synthesized

by Geelhaar *et al.* [17], and is distributed by Industrial Chemicals Division of Merck. Reducing the symmetry of tilted smectic phases by adding a chiral polar dopant to a host with an appropriate smectic phase results in ferroelectric LC mixtures. For the preparation of the smectic C host mixture, a 1,4-disubstituted cyclohexane derivative, substituted preferably by an additional axial nitrile group, was used. The non-chiral smectic C host composed of phenylpyrimidines and chiral biphenyl-cyclohexylcarbonitriles is doped with 10% of a chiral biphenyl-lactate-ether [17]. A high spontaneous polarization of $-29 \, nC \, cm^{-2}$ at 20°, a negative dielectric anisotropy for dielectric stabilization and a long helical pitch in the cholesteric phase (about $-60 \, \mu m$ at 80°C) are significant characteristics of this ferroelectric smectic mixture [18]. The negative sign before the helical pitch describes a left handed helical structure. The field needed to unwind the helix of a smectic C* liquid crystal is inversely proportional to the length of its pitch [8]. For easy unwinding of the helical structure on application of the voltage we have therefore chosen this material with a long pitch. Typical NMR spectra of ZLI-3654 are shown in figure 2.

The thermal behaviour of the material was investigated by polarizing microscopy (Amplival Pol-U microscope made by Carl Zeiss Jena) coupled with a heating stage. The phase sequence obtained was as follows:

$$Cr - 30°C \; S_C^* \; 62°C \; S_A \; 76°C \; Ch \; 86°C \; Iso.$$

The substance was contained in sandwich cells made from plates of ITO-coated glass separated by polyimide spacers in the range from 20–200 μm. The glass surfaces were cleaned, but not further treated. The layer thickness used in the cells is a compromise between the minimum thickness to achieve a sufficient sample signal and a maximum size to obtain a more or less bookshelf geometry.
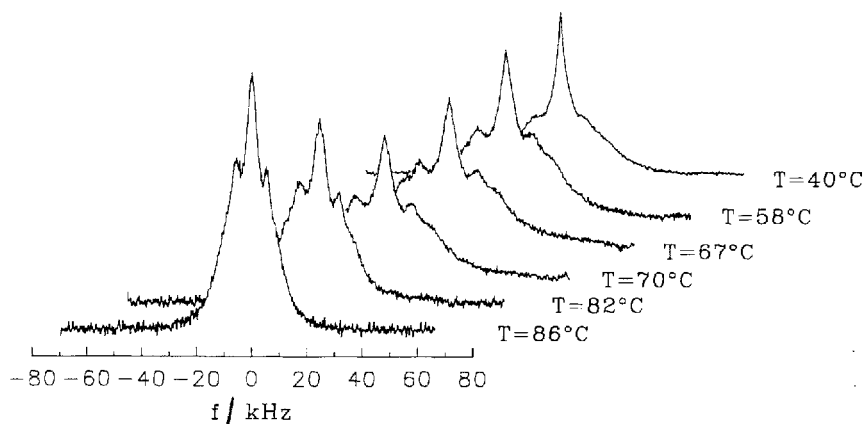
The cell was filled by capillary action, while the sample was kept 20 K above the clearing point for some minutes. An isotropic texture in the cells was checked by polarizing microscopy and proton NMR before applying the orientational procedure. A field strength between 0·005 and 5 MV m^{-1} was used. Short circuiting in the cell can occur at higher field strengths. The experimental setup is shown in figure 3.

The NMR spectra were obtained with a FKS 178 spectrometer working at a magnetic field of 1·4 T (60 MHz frequency for protons). The spectra were taken after a fast Fourier transformation of the FID. The length of the 90° pulse was about 1 μs. The sample temperature was controlled by use of a thermoclement (temperature error < 0·5°C). Temperature calibration was performed by observing the cholesteric to isotropic phase transition. Up to 8000 scans were accumulated for each spectrum to achieve a good signal-to-noise ratio.
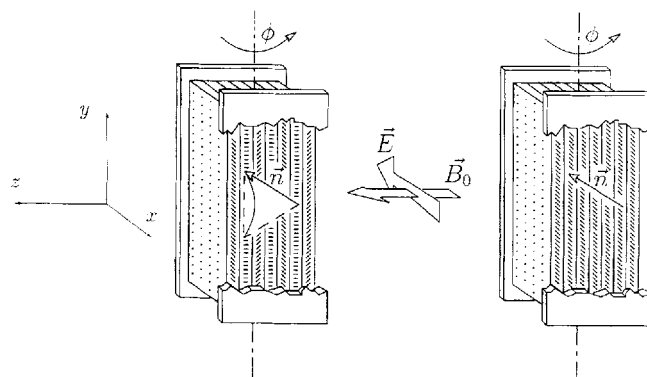

Figure 3. Sample geometry in the spectrometer and the transition into the switched state. The long axes of the molecules within the layers tend to be oriented in a specific preferred direction called the director and conventionally denoted by a unit vector **n**.

Figure 2. A seletion of typical spectra of ZLI-3654 dependent on the temperature.

4. Results and discussion

The orientational order parameter S of magnetically and electrically oriented samples was estimated. Typical angular dependences of the resonance line were measured in field preoriented layers in the bookshelf geometry and in ferroelectric switched samples. It was possible to measure the temperature dependence of the tilt angle of the mesogenic units by a numerical fit of the line width. The preparation of the bookshelf geometry was achieved by alignment of the mesogenic units in the B_0-field direction during slow cooling of the sample inside the spectrometer.

4.1. Magnetic and electric alignment

The alignment of the director along the B_0 direction has its origin in the anisotropic diamagnetic susceptibility $(\Delta\chi \approx 10^{-9}\,\mathrm{m^3\,kg^{-1}})$ mainly due to the biphenyl groups in the ZLI-3654 mixture. The smectic A phase can be aligned by cooling the sample slowly from the cholesteric phase. The diamagnetic anisotropy is positive and, therefore, the director tends to align parallel to the external magnetic field.

The spectra are dominated by the dipolar interaction between the *ortho*-protons of each benzene ring. A sharp central line in the spectra corresponds to the isotropic part of the sample, mainly of the unoriented protons of the alkyl chains in the molecules. By means of a strong electric field, well-oriented layers with a remarkable angular dependence of the line-width could be produced.

The dielectric anisotropy $\Delta\varepsilon$ is negative, and the director tends to align perpendicular to the external electric field. The magnetic field influence (1·4 T) is negligible on application of an electric field higher than $E = 0.5\,\mathrm{MV\,m^{-1}}$.

4.2. Ferroelectric switching in magnetically preoriented layers

The experiments were carried out as follows:

— The layer normal of the planar cell is arranged perpendicular to the strong magnetic B_0-field. A well-oriented sample in the bookshelf geometry was produced by cooling down $(1°\mathrm{C\,min^{-1}})$ the sample from the cholesteric phase to the S_C^* phase by magnetic orientation of the substance. The directors are arranged in a cone around the magnetic field direction.

— A direct current electric field was applied perpendicular to the axis of the helical structure. A ferroelectric switching was induced and was detected by measuring the angular dependence of the line width with variation of the angle ϕ.

Oriented layers stable over a long period of time were prepared by cooling the sample in the strong B_0 field to room temperature. The quality of the bookshelf geometry was checked by polarizing microscopy between crossed polarizers. The cell shows a typical fan-shaped texture of a S_C^* liquid crystal before the alignment procedure.

After the influence of the orientational B_0 field and cooling to room temperature, the sample has a stripe-shaped texture without any fans. Several papers have discussed models for the striped texture [19, 20], and it was usually found that the width of the stripes is approximately equal to the cell gap.

The alignment of the director by the electric field can be switched reversibly. This corresponds to the fact that the director field relaxes back to the initial direction (B_0 direction) when the E-field is switched off. The deformed angular dependence of the line width (see figure 4) of an unwound sample changed to a typical $(3\cos^2\phi - 1)$ function under the influence of an electric field; see also figure 5. The directors form a single angle, the tilt angle θ, with respect to the B_0 field and the smectic layer normal, respectively.

4.3. Simulation of the line width and derivation of the tilt angle in the S_C^* phase

In the S_C^* phase, the directors are tilted and distributed over a cone around the normal of the smectic layers because of the helical structure. It is known that the helical structure of liquid crystals formed by a S_C host and a chiral dopant are preserved in magnetic fields [21]. This fact was confirmed by our measurements on ZLI-3654 in a magnetic field of 1·4 T.

The directors are distributed over a cone about the B_0 direction and do not form a single angle with respect to the magnetic field. For the simulation, a conical distribution of the director around a preferred axis in the plane of the magnetically pre-oriented cell was assumed. The azimuthal angle of the cone was twice the tilt angle θ. The initial situation, corresponding to a rotation angle $\phi = 0°$ of the sample, is depicted in figure 6. A large number N of proton internuclear vectors with $|\mathbf{r}_{ik}| = 2.45\,\text{Å}$ is arranged on a cone around the z axis. The axis of the cone is rotating in Z steps around the y axis in the x–z plane of the frame. The index i chooses one vector from this argument. The k index describes the rotation of the vector around the y axis. With

$$\mathbf{r}_{ik}(\theta, \phi_k) \qquad (8)$$

the angle of the vector relating to the z axis is

$$\beta_{ik} = \arccos\left(\frac{r_{ik}(z)}{[(r_{ik}(x))^2 + (r_{ik}(y))^2 + (r_{ik}(z))^2]^{1/2}}\right), \quad (9)$$

where $r_{ik}(x)$, $r_{ik}(y)$ and $r_{ik}(z)$ mean the x-, y- and z-components of the vector $\mathbf{r}_{ik}$. This vector induces a

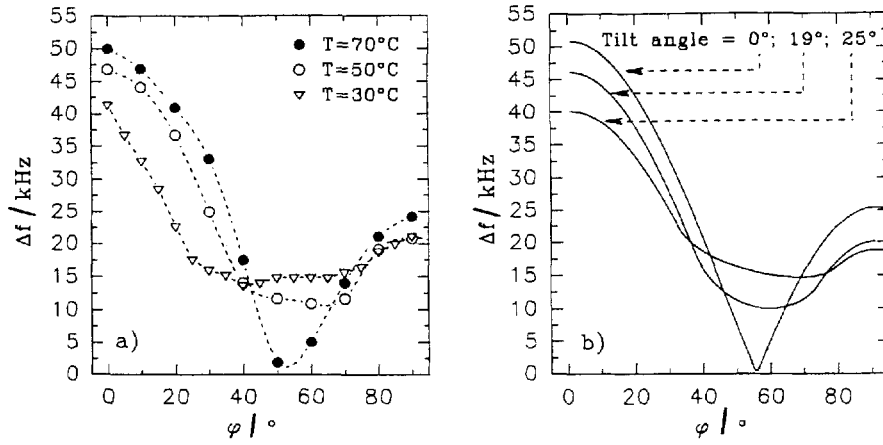Figure 4. The measured (*a*) and the simulated (*b*) angular dependence of the line-width of a sample at different temperatures in bookshelf orientation.
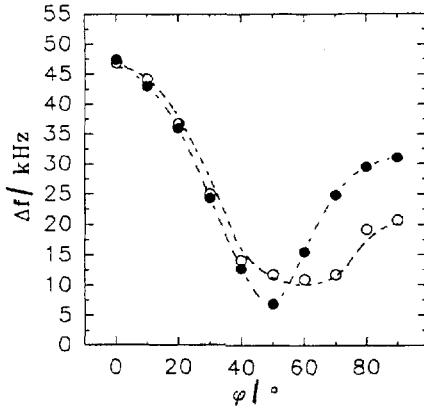
Figure 5. A 100 μm sample in the unswitched (○) and in the ferroelectric switched state (●), $E = 2 \cdot 5$ MV m^{-1}, $T = 50°C$.

splitting

$$\Delta v_{ik} = \frac{3\mu_0}{8\pi^2} \frac{\gamma^2 \hbar}{\langle r^3 \rangle} \frac{1}{2}(3\cos^2 \beta_{ik} - 1)S \qquad (10)$$

of the resonance line. The line width dependence on the angle of rotation ϕ and the tilt angle θ of the director is now given by

$$\Delta f(\phi, \theta) = \frac{1}{N} \sum_{i=1}^{N} \sum_{k=0}^{Z} \frac{3\mu_0}{8\pi^2} \frac{\gamma^2 \hbar}{\langle r^3 \rangle} \frac{1}{2}(3\cos^2 \beta_{ik} - 1)S + C, \qquad (11)$$

where C is a constant to change from Δv to Δf. Within the experimental error, the simplest way to determine C is to use Δf from the measurements with

$$C = \min \{\Delta f\}. \qquad (12)$$

By use of equation (11), it was possible to fit the computed data of the angular dependence of the line width to the measured data by the least square method.
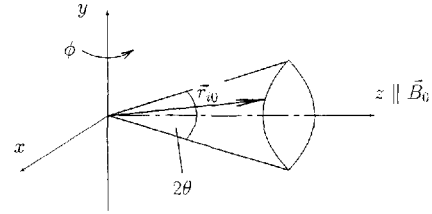

Figure 6. Geometry of the r_{ik} distribution and the coordinate frame used by numerical calculation.

The most sensitive fit parameter was the tilt angle θ of the conical director distribution. Some representative results are shown in figure 4. The computed temperature dependence of the tilt angle is in good accordance with the optical data published by Merck (see figure 7). Results of the NMR tilt angle are fitted to the equation

$$\theta = \theta_0(T_C - T)^{\alpha'} \quad \text{for } T < T_C, \qquad (13)$$

where $\alpha' = 0 \cdot 25$. Based on the results of the mean-field theory, α lower than $0 \cdot 5$ implies the existence of a
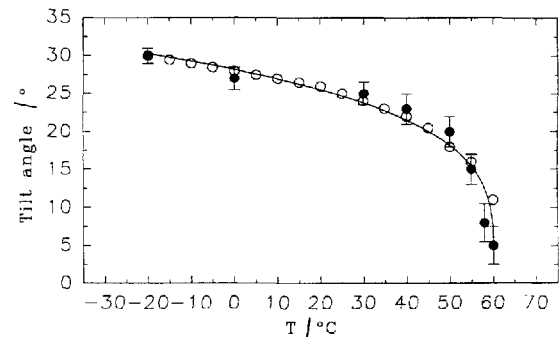

Figure 7. Plot of the temperature dependence of the tilt angle of ZLI-3654; the continuous line fits to equation (14) with $\alpha' = 0 \cdot 25$, (○) data from Merck [14], (●) the computed data and the error of the calculation.
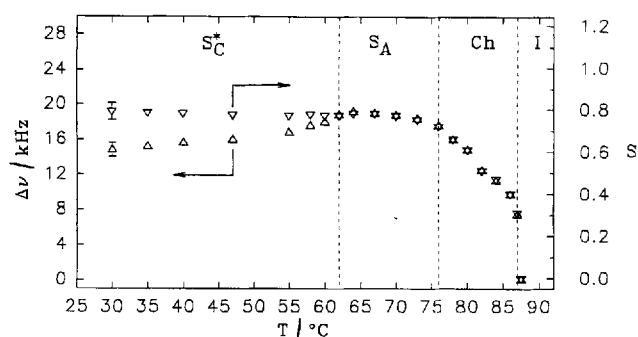
Figure 8. The orientational order parameter S ($\triangledown$) and the line splitting Δv ($\triangle$) versus temperature.

biquadratic coupling and the piezoelectric coupling between the tilt angle θ and the spontaneous polarization P_S [22].

The degree of orientational order S in equation (11) is the second parameter of fitting. Another way to determine S in the smectic C^* phase is the following. Since the two phenyl rings have the same order parameter within experimental error, its temperature dependence was determined using the line splitting of the resonance line (see figure 8). The S_A–Ch transition is, from the viewpoint of symmetry, a phase transition of the first order, but very weak. The transitional entropy is unreliable and the orientational order parameter S is changing too. Our NMR method is not sensitive enough to measure this variation of the S parameter in the range of 5%.

By using the optical tilt angle of the director in the temperature range of the S_C^* phase, it was also possible to describe the temperature dependence of the orientational order parameter S in the ferroelectric phase. In this region, the increase of the tilt angle on decreasing the temperature is reflected in a reduction of the line splitting. This effect compensates the increase of the line splitting caused by the temperature dependence of the orientational order parameter S.

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